High-pressure amorphous nitrogen

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The phase diagram and stability limits of diatomic solid nitrogen have been explored in a wide pressure-temperature range by several optical spectroscopic techniques. A narrow-gap semiconducting phase η has been found to exist in a range of 80–270 GPa and 10–510 K. The vibrational and optical properties of the η phase produced under these conditions indicate that it is largely amorphous and back transforms to a new molecular phase. The band gap of the η phase is found to decrease with pressure indicating possible metallization by band overlap above 280 GPa.

Despite early theoretical predictions for a transformation of nitrogen to a monoatomic state,[1-3] reliable experimental evidence became available only quite recently.[4,5] Optical spectroscopy, visual observations, and electrical conductivity measurements showed that the material transforms to a semiconducting nondiatomic phase at 150 GPa (190 GPa at 80 K).[4,5] The transition to the nonmolecular state was predicted to be hindered by a large energy barrier and accompanied by a large volume discontinuity and hysteresis.[2,3] The latter was confirmed by visual observations which indicated that the high-pressure phase can be possibly preserved on release of pressure at low temperatures.[5]

Characterization of the high-pressure phase (called η here) still remains an important issue because of the lack of structural studies and systematic spectroscopic data at different P-T conditions. Optical absorption spectra[4] reveal the presence of a low-frequency logarithmic Urbach tail[6] and a higher-energy region, which obeys the empirical Tauc law.[7] This type of absorption edge is typical for amorphous semiconductors (see Ref. 8). Although being quite diagnostic, this observation still requires confirmation, as a highly disordered high-pressure structure is consistent with the nature of the transformation; i.e., a large volume change at a reconstructive phase transition can cause large shear stresses because of inhomogeneous nucleation of the high-pressure phase (see Ref. 9). Moreover, experiments demonstrate that two phases coexist in a wide pressure range (at 300 K),[4] thus making characterization of the η phase even more difficult. Here we present new optical data over a wide P-T range indicating that high-pressure nonmolecular phase is a largely amorphous, narrow-gap semiconductor to at least 268 GPa. We examine the stability limits of the diatomic molecular state and present evidence for new transformations, including metallization by band overlap above 280 GPa.

Four experiments were performed at room temperature with the maximum pressures varied from 180 to 268 GPa. Above 200 GPa pressure was determined using tunable red lines of Ti:sapphire laser combined with a time resolving technique (Fig. 1). For low-temperature measurements we used a continuous-flow He cryostat, which allowed infrared and *in situ* Raman and fluorescence measurements.[10] High-temperature Raman and visible transmission measurements

were performed with an externally heated cell.[11] In this case, infrared measurements were done on samples quenched to room temperature.

Figure 2 shows representative IR and visible transmission spectra demonstrating the effect of temperature on the semiconducting optical edge characteristic of the η phase. The spectra presented correspond to conditions when no molecular phase is present in the sample as determined from vibrational spectroscopy (see below). No variation of the shape and position of the band gap can be detected from transmission spectra at different temperatures and constant pressure of 200 GPa. Figure 2(b) shows that the low-energy portion of the spectra plotted on a logarithmic scale (Urbach plot) has a constant slope (Γ) in a 10–200 K range. This also agrees with 300 K data,[4] thus showing that Γ is not temperature dependent. Similar spectra have been reported for amorphous phosphorus at zero pressure.[13] This is typical for solid amorphous semiconductors,[8] because the random microfield is caused by static disorder in the system as opposed to crystalline materials[6] where the vibrations generate a temperature-dependent dynamical disorder.

Determination of the band gap from our data is a complicated issue, because there is no characteristic feature of the
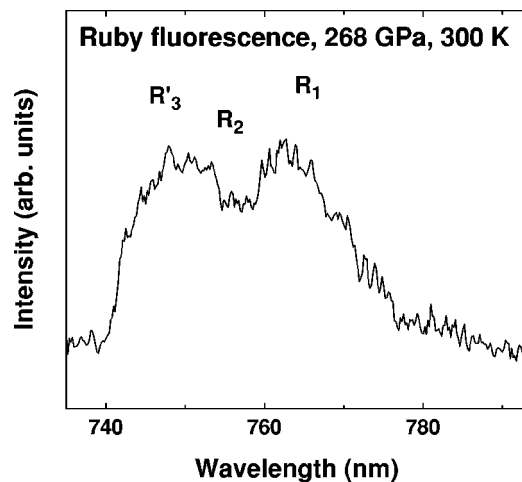

FIG. 1. Ruby fluorescence spectrum at pressure 268 GPa and 300 K. Ruby was excited with the 730 nm line of a Ti:sapphire laser.
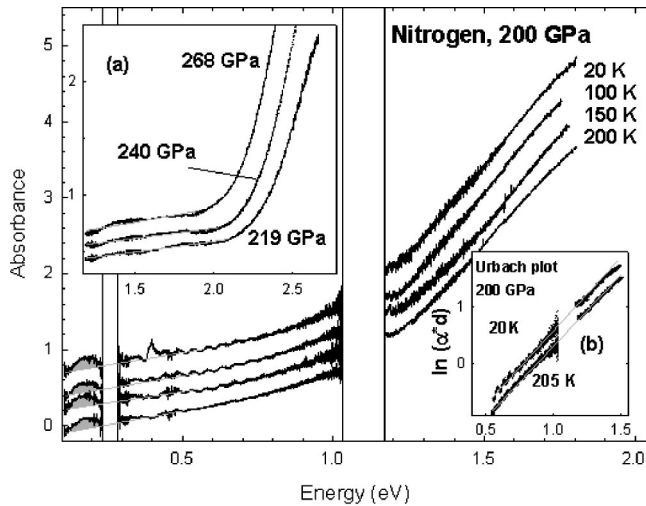
FIG. 2. Transmission spectra of N_2 as a function of temperature. Spectra are shifted vertically for clarity. The characteristic peak of the η phase is shaded. Inset (a) shows the pressure dependence of the absorption spectra of N_2 at very high pressures and room temperature. Gray lines represent the Tauc fits to the spectra in an appropriate spectral range. The determination of the energy gap from these measurements is obscured by additional losses caused by the presence of a fine ruby powder in the chamber. The high-energy absorption edge is most probably due to stress-induced absorption of diamond anvils (Ref. 12). (b) Urbach plots at 200 GPa and different temperatures (shifted vertically). Gray lines are guides to the eye.

spectra which can be associated with the band gap (e.g., Ref. 14). This is especially important for our measurements, since we essentially deal with samples of various thickness (which is a function of anvil geometry and pressure). As the result, visual observations of the sample above 230 GPa showed that it is red or yellowish in transmission and black in reflection, which is consistent with the semiconducting state. The color of the sample (compare with the observations of dark nitrogen in Refs. 4, 5, 15, and 16) may be explained by its thickness (of the order of 1 μm) compared to the samples brought to 150 GPa (up to 5 μm). At the highest pressure (268 GPa), visible transmission spectra clearly show the presence of the fundamental absorption edge characteristic of semiconductors [Fig. 2(a)]. This result is in agreement with direct electrical measurements performed to 240 GPa.[5]

The high-energy absorption edge, which can be observed in this case, corresponds to electronic transitions between extended states (unlike Urbach absorption, which is presumably caused by transitions from localized to extended states). Extrapolation of the absorption spectra plotted as $(h\nu\alpha)^{0.5}$ versus $h\nu$ gives the value of optical gap.[7] These values at different pressures are shown in Fig. 3. Note that data from different experiments agree, despite the different sample thickness and the fact that some of the data are taken on pressure release in a metastable pressure region (see below). We observed a monotonic redshift of the band gap with pressure [see also Fig. 2(a)]. The pressure dependence of the band gap is sublinear mainly due to contribution from the points obtained on decompression. The extrapolation of the
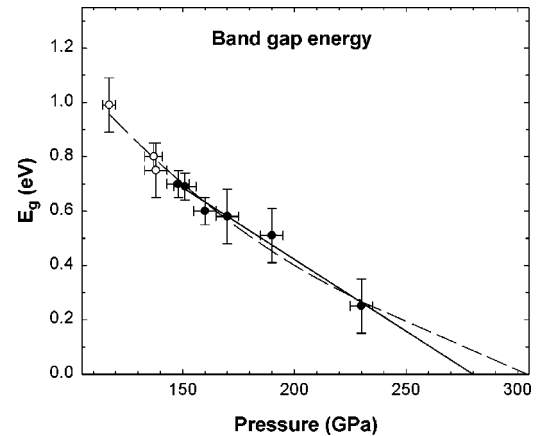

FIG. 3. Band gap of the η phase as a function of pressure. Solid circles represent increasing pressure and open circles decreasing pressure. Linear and quadratic extrapolations are shown as dashed lines.

band gap values gives metallization at pressures slightly above 300 GPa. Linear extrapolation of this curve to higher pressures (not taking into account points obtained upon decompression) gives a value of 280 GPa.

We now present temperature measurements of the vibrational properties of the η phase. Type II diamonds were used for mid-IR measurements to avoid interference with the characteristic absorption of the sample. The representative absorption spectra at different temperatures (see Fig. 2) clearly show the presence of a broad 1700 cm^{-1} IR band (compare with Ref. 4). Its presence was also observed in the sample heated to 495 K at 117 GPa (see below). The position of the band and its damping (if fitted as one band) does not depend on pressure and temperature within the error bars.

The Raman spectrum of the η phase obtained on heating (see below) does not show any trace of the molecular phase [see Fig. 4(b)]. Careful examination of the spectrum in this case showed a weak broadband at 640 cm^{-1} in agreement with the data of Ref. 4 and a shoulder near 1750 cm^{-1} [both indicated by arrows in Fig. 3(b)]. The latter may indicate the presence of a second Raman peak close to the position of the observed IR band, but can also be due to Raman spectra in the stressed diamond. The broad two-peak structure of the phonon spectrum of the material is consistent with its amorphous nonmolecular nature.[17] For an amorphous state, the spectrum observed would closely resemble a density of phonon states[18] with the maxima corresponding roughly to the zone boundary acoustic and optic vibrations of an underlying structure.[19] The only lattice dynamics calculations for hypothetical high-pressure crystalline phases of nitrogen are available for the cubic gauche phase,[20] and calculated phonon frequencies are in good agreement with our measurements. The vibrational spectroscopy and band gap structure indicate the absence of a long-range order. The material can still possess some short-range order, for example, related to pyramidal coordination of nitrogen atoms. The absence of long-range order can be due to structural flexibility because each atom forms bonds with only three other atoms out of six nearest neighbors.[19]
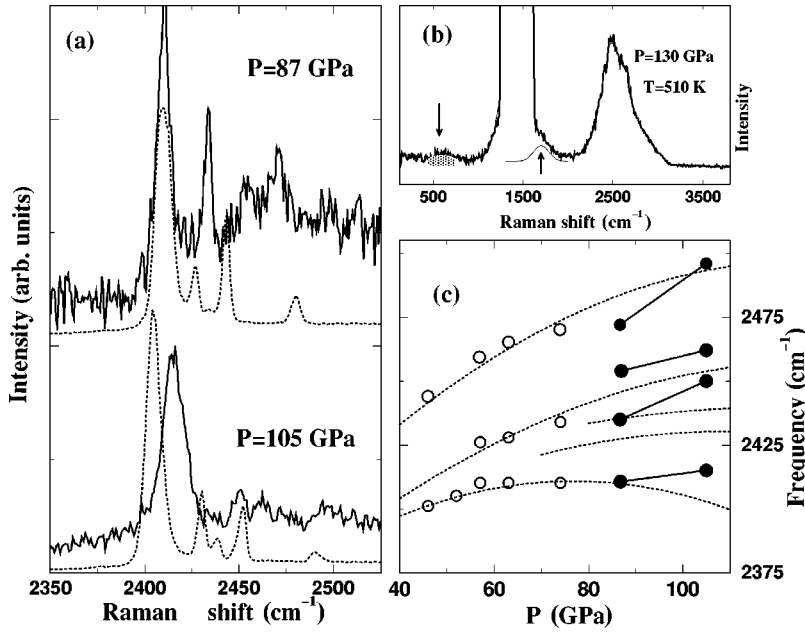
FIG. 4. (a) Raman spectra in the ζ (dotted lines) and ζ' (solid lines) phases. (b) Raman spectra of the η phase (indicated by arrows); the fitted curve shows a peak at 1700 cm^{-1}. (c) Raman shifts of molecular phases vs pressure. Dotted lines represent shifts on compression. Solid lines and full circles represent shifts on decompression in ζ' phase; open circles correspond to ϵ phase.

We probed the forward and reverse transformations of the molecular to the η phase in different regions of P-T space. We used IR transmission spectra as diagnostics of the degree of transformation to the nonmolecular phase. The absence of IR bands corresponding to vibrons and lattice modes of the molecular phase[4] was used as a criterion. Since both the molecular and nonmolecular phases are transparent in the mid-IR, the amount of the phase present is simply *proportional* to the amplitude of the corresponding IR peaks. This is unlike the situation with Raman spectra which are attenuated by absorption the η phase. We examined the transformation at 205 K and elevated pressures and found that it starts at 155 GPa and is completed at 185 GPa. This is shifted to higher pressures compared to our 300 K data[4] and is in agreement with the trend reported in Ref. 5. The sample has been cooled down to 10 K at 200 GPa and warmed up after subsequent release of pressure at 130–150 GPa. IR and visible transmission spectra and Raman spectra clearly showed the persistence of the η phase without any reverse transformation down to 120 GPa. At this point the pressure dropped to 87 GPa and the sample transformed instantaneously back to a transparent phase (called ζ' here). The molecular nature of this phase is confirmed by its Raman spectrum [Fig. 4(a)], although the positions of the vibron lines do not correspond to those observed on pressure increase [Fig. 4(c)]. This means that the amorphous phase backtransforms to a molecular phase which differs from the one observed on upstroke. On further release of pressure (to 60 GPa) we observe the Raman spectra which are similar to those of ζ or ϵ phases in positions and intensities of vibron peaks. The quality of the spectra (on pressure release, the sample thins down, leading to a considerable loss of intensity) does not allow one to establish the presence or absence of the weaker vibron modes characteristic of the ζ phase and unambiguously determine whether the ζ' phase backtransforms to the ζ or ϵ phase.

In the heating experiment we first exposed the sample to 495 K at 117 GPa. The effect of temperature caused a gradual transformation (starting at 450 K) similar to that observed at 300 and 200 K. The comparison of Raman modes revealed more than a tenfold decrease of intensity in the Raman vibrons and no observable lattice modes. Quenching of the sample to room temperature did not change the color
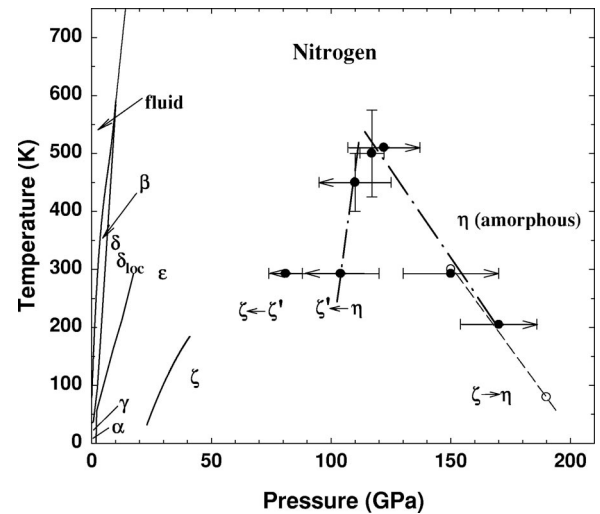

FIG. 5. Phase diagram of nitrogen in a wide P-T range. Solid circles, dash-dotted lines, and arrows are the data from this work. Open circles and the dashed line are from visual observations of Ref. 5. Arrows show the paths along which the transformation boundaries were crossed. The length of the arrow represents the width of the two-phase region or pressure uncertainty (on a pressure release). Phase boundaries at low pressures are from Refs. 21 and 22). The phase boundaries for α, γ, and δ_{loc} phases are not shown. There is evidence for further pressure-induced transformations of the high-pressure molecular ζ phase but the products are believed to be closely related (Refs. 15 and 23).

and visible absorption spectra. Surprisingly, the infrared spectra revealed the presence of molecular vibrons, indicating an incomplete transformation (about 30% of the nonmolecular phase judging from the infrared activity). During the second heating the sample was completely transformed to the η phase. Then the pressure was dropped to 105 GPa at 460 K, causing an instantaneous reverse transformation to a transparent molecular phase. The spectral positions of the bands and their number do not correspond to those observed at this pressure on compression but are similar to those obtained during the unloading at 300 K (see above). Increasing pressure to 135 GPa at 510 K drove the direct transformation into the η phase again.

Figure 5 summarizes our data for the phase diagram of nitrogen obtained in a course of extensive P-T measurements. Substantial hysteresis is observed for the transformation from and back to the molecular phase, so the observed curves should be treated as kinetic boundaries. For a direct transformation, our data are in good agreement with the results of visual observations of Ref. 5. Our high-temperature data show that the hysteresis becomes quite small at temperatures above 500 K. There is large hysteresis at lower temperature such that the molecular ζ phase can be metastably retained beyond the ζ-ζ' boundary (above approximately 100 GPa; see also Ref. 5). Thus, observation of another molecular phase (ζ') in this P-T conditions means that this phase is either kineticaly favored or thermodynamically stable with respect to the ζ phase.

If the potential barrier between two crystalline phases is high (molecular dissociation is required in our case), the transition may be preempted by a transformation to a metastable phase, which may be amorphous.[24] This defines an intrinsic stability limit (e.g., spinodal) for the diatomic molecular state of nitrogen. In view of the amorphous component of the higher-pressure phase, the transition may be considered as a type of pressure-induced amorphization. As such, the transformation boundary could track the metastable extension of the melting line of the molecular phase, and if so, it should have a negative slope (consistent with negative ΔV and positive ΔS for a transition to dense amorphous state[24]). Alternatively, one can view this in terms of an intrinsic (elastic or dynamical) instability of the structure of the molecular solid. In this sense, the behavior of the material parallels other amorphizing systems that undergo coordination changes (see Ref. 25).

[1] A. K. McMahan and R. LeSar, Phys. Rev. Lett. **54**, 1929 (1985).

[2] R. M. Martin and R. J. Needs, Phys. Rev. B **34**, 5082 (1986).

[3] C. Mailhiot, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14 419 (1992).

[4] A. F. Goncharov, E. A. Gregoryanz, H. K. Mao, Z. Liu, and R. J. Hemley, Phys. Rev. Lett. **85**, 1262 (2000).

[5] M. I. Eremets, R. J. Hemley, H. K. Mao, and E. Gregoryanz, Nature (London) **411**, 170 (2001).

[6] F. Urbach, Phys. Rev. **92**, 1324 (1953).

[7] J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi **15**, 627 (1966).

[8] N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials*, 2nd ed. (Clarendon Press, Oxford, 1979).

[9] R. Jeanloz, J. Geophys. Res. **92**, 10 352 (1987).

[10] A. Goncharov, V. Struzhkin, R. Hemley, H. Mao, and Z. Liu, in *Science and Technology of High Pressure*, edited by M. H. Manghnani, W. J. Nellis, and M. F. Nicol (Universities Press, Hyderabad, India, 1999), Vol. 1, pp. 90–95.

[11] Y. Fei, in *Mineral Spectroscopy: A Tribute to Roger G. Burns*, edited by M. D. Dyar, C. McCammon, and M. W. Schafer (Geochemical Society, Houston, 1966), p. 243.

[12] Y. K. Vohra, in *Recent Trends in High Pressure Research*, edited by A. K. Singh (Oxford & IBH, Calcutta, 1991), p. 349.

[13] L. J. Pilione, R. J. Pomian, and J. S. Lannin, Solid State Commun. **39**, 933 (1981).

[14] S. Knief, Phys. Rev. B **59**, 12 940 (1999).

[15] R. Reichlin, D. Schiferl, D. Martin, C. Vanderborgh, and C. Mills, Phys. Rev. Lett. **55**, 1464 (1985).

[16] P. M. Bell, H. K. Mao, and R. J. Hemley, Physica B & C **139&140B**, 16 (1986); R. J. Hemley (unpublished).

[17] Y. K. Vohra, H. Hia, H. Luo, and A. Ruoff, Appl. Phys. Lett. **57**, 1007 (1990).

[18] M. H. Brodski, in *Light Scattering in Solids*, edited by M. Cardona, Vol. 8 Topics in Applied Physics (Springer-Verlag, New York, 1983).

[19] Theoretical calculations (Ref. 3) reveal several candidates for the high-pressures phase. All three-coordinated structures can be obtained by distortion of a simple cubic phase (sixfold coordinated which is unstable) and are related to phonon instabilities in different high-symmetry points of the Brillouin zone (Ref. 20).

[20] T. W. Barbee III, Phys. Rev. B **48**, 9327 (1993).

[21] D. A. Young, C. Zha, R. Boehler, J. Yen, M. Nicol, A. Zinn, D. Schiferl, S. Kinkead, R. Hanson, and D. Pinnick, Phys. Rev. B **35**, 5353 (1987).

[22] R. Bini, M. Jordan, L. Ulivi, and H. Jodl, J. Chem. Phys. **108**, 6849 (1998); R. Bini, L. Ulivi, J. Kreutz, and H. Jodl, *ibid.* **112**, 8522 (2000).

[23] H. Olijnyk and A. P. Jephcoat, Phys. Rev. Lett. **83**, 332 (1999).

[24] For recent reviews see S. M. Sharma and S. K. Sikka, Prog. Mater. Sci. **40**, 1 (1996); P. Richet and P. Gillet, Eur. J. Mineral. **9**, 907 (1997).

[25] R. J. Hemley, A. Jephcoat, H. Mao, L. Ming, and M. Manghnani, Nature (London) **334**, 52 (1988); J. Badro, J.-L. Barrat, and P. Gillet, Europhys. Lett. **42**, 643 (1998). This includes the likelihood that material produced on compression is heterogeneous (i.e., partly crystalline); see R. J. Hemley, J. Badro, and D. M. Teter, in *Physics Meets Mineralogy*, edited by H. Aoki, Y. Syomo, and R. Hemley (Cambridge University Press, Cambridge, England, 2000), p. 173.